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Viscoelasticity of a Solution of Star-Branched Polystyrene

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The relaxation modulus, $G(t, \gamma)$, at finite magnitude of shear, γ , was measured for a solution of a star-branched polystyrene, composed of four chains with molecular weight M_b each connected at one end at a point. The result was compared with that for a linear polymer with molecular weight $2M_b$, i.e., with the same end-to-end chain length as the branched polymer. The stress relaxation of the branched polymer was much slower than that of the linear polymer. On the other hand, the function $h(t, \gamma) = G(t, \gamma)/G(t, 0)$ was approximately the same for two polymers. The observation may be in accord with the tube model theory of polymer entanglement; the branch point should hinder the sliding motion of the chain as a whole along the tube-like cage formed by surrounding chain molecules while it should not disturb the shrink of chain along the tube, which gives rise to the nonlinear characteristics of relaxation modulus.

KEY WORDS: Branched polymer/ Polymer chain entanglement/ Stress relaxation/ Nonlinear viscoelasticity/

INTRODUCTION

In concentrated solutions or melts of polymers, the motion of a polymer chain is hindered and retarded by entanglement with other polymer chains.¹⁾ The stress relaxation under constant deformation proceeds very slowly over a certain range of time. The stress finally begins to decrease as the polymer chain moves a considerable distance sliding along the entanglement points. An example of stress relaxation measurement²⁾ is shown in Fig. 1. Here the relaxation modulus, $G(t, \gamma)$, is defined as the ratio of the shear stress to the magnitude of shear, γ , after a shear deformation is applied instantaneously at time $t=0$. The limiting value of $G(t, \gamma)$ at $\gamma \rightarrow 0$, represented by the curve at the top, is usually denoted as $G(t)$. As the strain, γ , becomes larger, the relaxation modulus, $G(t, \gamma)$, becomes to depend on γ . The nonlinear behavior can be more closely investigated with a function

$$h(t, \gamma) = \frac{G(t, \gamma)}{G(t)} \quad (1)$$

This function starts from unity, decreases with time, and levels off at a certain time denoted as τ_k . Curves for various γ values level off at approximately the same time. The final value of $h(t, \gamma)$, denoted as $h(\gamma)$ hereafter, decreases with increasing γ .

The most widely accepted theory for the motion of a polymer in entangled system

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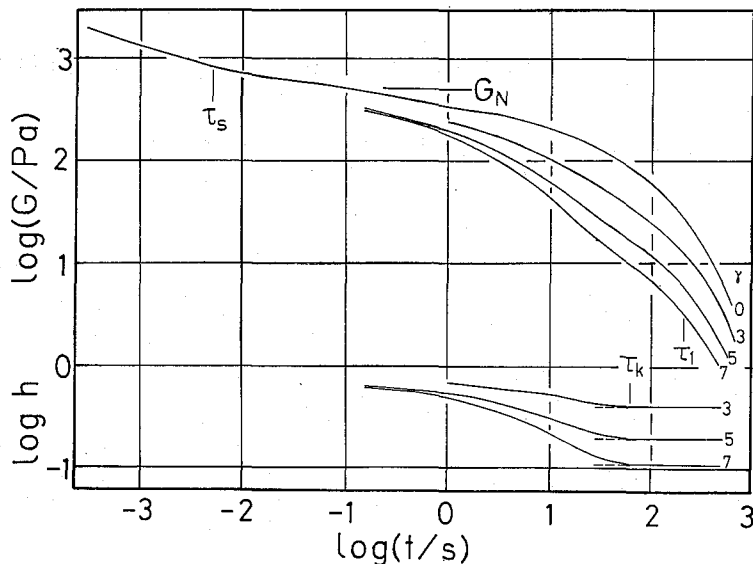


Fig. 1. Relaxation modulus, $G(t, \gamma)$, and function $h(t, \gamma)$ for solution of poly (α -methylstyrene) in Aroclor at 30°C; $M=6.85 \times 10^6$ and $c=0.071 \text{ gcm}^{-3}$.

is the tube model theory of de Gennes³⁾ and Doi and Edwards.⁴⁾ In this theory, a polymer molecule is assumed to be confined in a tube-like cage formed by surrounding chains. The molecule is allowed to slide back and forth along the tube and to come out of the ends of the tube; the loop-wise extrusion of the molecule through the tube wall is not allowed. The motion of the chain along highly twisted tube, called the reptation by de Gennes,³⁾ is very slow and it takes quite a long time for the chain molecule to lose the memory of the original shape. This time is supposed to correspond to the longest relaxation time, τ_1 , of the relaxation modulus. On the other hand, the molecular motion of the distance of the order of the tube diameter is not hindered by the wall and proceeds in a relatively short time, τ_s . The time gap between τ_s and τ_1 corresponds to the plateau region where the relaxation is very slow.

In the tube model theory, the origin of nonlinear viscoelasticity is attributed to the shrink of the highly extended chain toward its equilibrium length along the tube.⁴⁾ This process is estimated to be much faster than reptation motion. Thus a part of the stress is lost before the final relaxation of stress begins. This picture is in accord with the observed behavior of the function $h(t, \gamma)$ shown in Fig. 1. The final value, $h(\gamma)$, of the function $h(t, \gamma)$ obtained by assuming the shrink of chain was in quantitative agreement^{4,5)} with the observed values.^{6,7)} The theory tells that the characteristic time for the shrink process should be proportional to $\tau_s N^2$ where N is the number of entanglements per molecule. The characteristic time τ_k , supposedly corresponding to the end of the shrinking process, was proved to be proportional to $\tau_s N^2$ irrespective of the polymer species, molecular weight, and concentration.²⁾ Thus the viscoelasticity of linear polymers is described fairly well with the tube model theory.

Now we consider a star-branched polymer, i.e., a polymer composed of f chains of

molecular weight M_b , each connected at one end at a point. For such a polymer, the sliding motion back and forth along the tube is impossible because of the hindrance at the branch point. The stress relaxation should proceed through some other, much slower, type of molecular motion.⁸⁾ On the other hand, the shrink of chain will not be much hindered by the branch point located at the center of molecule. Suppose we compare the stress relaxation of the star-branched polymer with that of a linear polymer with the molecular weight $2M_b$. We expect that the relaxation time of the former is longer than that of the latter while the function $h(t, \gamma)$ is essentially the same for both polymers. We examine this prediction in the present paper.

EXPERIMENTAL

A star-branched polystyrene with $f=4$ was synthesized by coupling polystyryl anion with 1, 2-bis (trichlorosilyl) ethane. The solvent was benzene and the initiator for the anionic polymerization was sec-butyllithium. The crude product was fractionated repeatedly in benzene-methanol system until the gel permeation chromatogram became sufficiently sharp. As determined with the gel permeation chromatography and light scattering method, the molecular weight of the primary polymer, M_b , was 6.62×10^5 and that of the branched polymer was 2.65×10^6 . The ratio of the weight average to the number average molecular weight, M_w/M_n , of the branched polymer was 1.06.

A linear polystyrene, a standard sample F8 from Toso Ltd., was used for comparison; $M_w=1.26 \times 10^6$ and $M_w/M_n=1.05$. The molecular weight is approximately equal to $2M_b$.

The stress relaxation measurements were performed for 15% solutions of two polymers in Aroclor 1248, a polychlorinated biphenyl supplied from Monsanto Chemical Co. Notations B and L hereafter refer to the solutions of the branched polymer and the linear polymer, respectively.

The relaxation modulus was measured with an apparatus of cone-and-plate type. The details of apparatus were reported elsewhere.⁹⁾ All the measurements were performed at 30°C.

RESULTS AND DISCUSSION

Linear Viscoelasticity

The relaxation modulus at infinitesimal strain, $G(t)$, is shown in Fig. 2. Evidently the stress relaxation of the solution of branched polystyrene (B) is much slower than that of the linear polymer (L). The longest relaxation time of B is about three times as large as that of L. By a close inspection, one may note that the drop at the long time end, e.g. at the level of $G=10$ Pa, for the branched polymer is not as sharp as that for the linear polymer. This behavior implies that a small fraction of the segments keeps on contributing to the stress for a very long time in the case of branched polymer as predicted by the Doi-Kuzuu theory.⁸⁾ It takes a long time for the orientation of segments near the branch point to become random. This is not the case for the linear

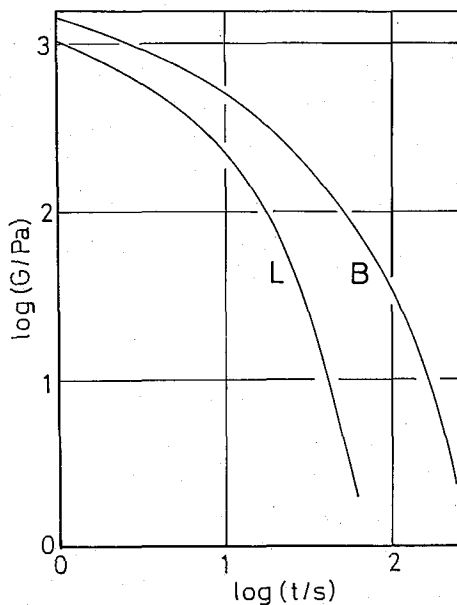


Fig. 2. Linear relaxation modulus, $G(t)$, for solutions of branched (B) and linear (L) polystyrenes.

polymer; the relaxation modulus at long time can be approximated by a single exponential decay function and drops sharply in accord with the tube model theory.⁴⁾

Nonlinear Viscoelasticity

The relaxation modulus at finite strain, $G(t, \gamma)$, for the solution of branched polymer is shown in Fig. 3. The time range apparently corresponds to long time end of Fig. 1. By comparison, one sees that the relaxation modulus of the branched polymer is qualitatively similar to that of the linear polymer.

The function $h(t, \gamma)$ is shown in Fig. 4 for solutions of the branched polymer (circles) and the linear polymer (solid lines). Obviously the data for the two systems overlap with each other over a wide range of time, $t < 10$ s, in which the decrease of the function $h(t, \gamma)$ is almost completed. The agreement between the two polymers may be quite impressive if one compares these results with the dashed lines for a linear polymer with the same molecular weight as the branched polymer. The agreement between the branched polymer and the linear polymer with the molecular weight $2M_b$ is in accord with the prediction based on the shrink of extended chains.

At longer times, the function $h(t, \gamma)$ for the linear polymer levels off while that for the branched polymer keeps on decreasing slowly and then levels off. Thus the function $h(t, \gamma)$ is not completely the same for the two polymeric systems. The final value, $h(\gamma)$, for the branched polymer is about 20% lower than that for the linear polymer when the strain, γ , is large.

The quantity $h(\gamma)$ is shown in Fig. 5. Here the circles represent the result for the solution of branched polymer. The line L represents the average of the many results

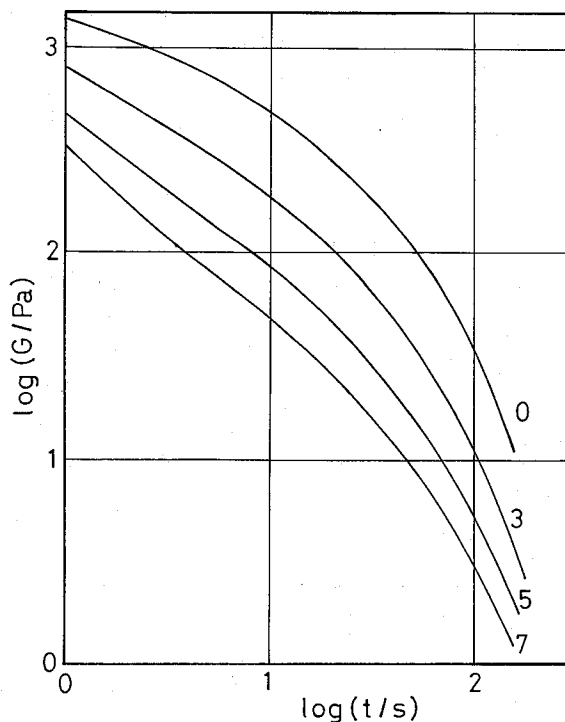


Fig. 3. Relaxation modulus, $G(t, \gamma)$, for solution of branched polymer B. Values of γ are given in figure.

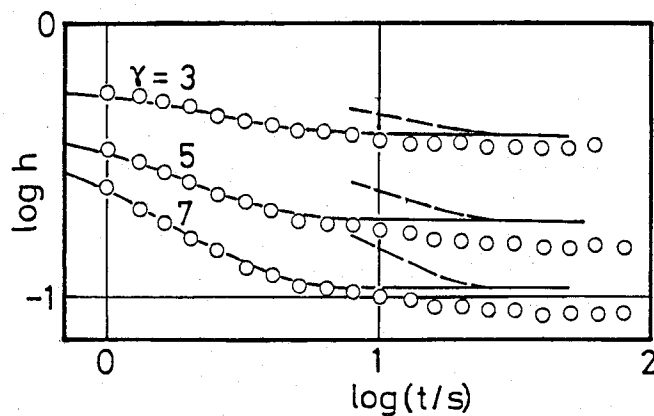


Fig. 4. Function $h(t, \gamma)$ for solutions of branched polymer (circles) and linear polymer L (solid lines). Dashed line is for linear polymer with the same molecular weight as branched polymer.

for solutions of linear polymers.^{2,6,8)} The result for the linear polymer in the present study lies on the line L. The line marked DE represents the theoretical result of Doi and Edwards⁴⁾ based on the concept of the shrink of chain. It may be noted that the experimental result for the branched polymer agrees very well with the theoretical result.

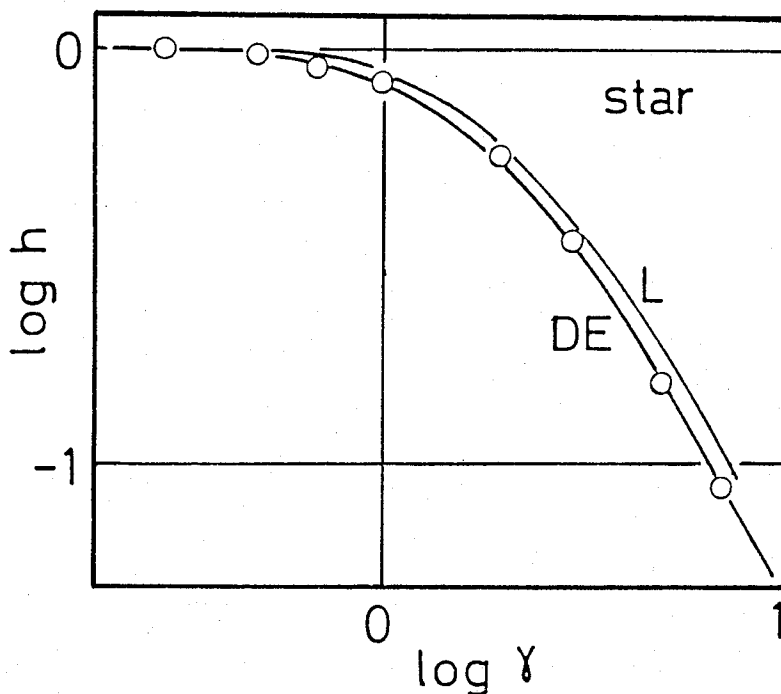


Fig. 5. Function $h(\gamma)$ for sample B(circles). Lines L and DE represent, respectively, average results for linear polymers and theoretical prediction due to Doi and Edwards.

Further Comments

The results shown in Figs. 2 and 4 may be sufficient to conclude that the prediction given in the introduction section is experimentally substantiated; the stress relaxation is slower for the star-branched polymer than for the linear polymer having the same end-to-end length while the nonlinear viscoelasticity, represented by the function $h(t, \gamma)$, is approximately the same for the two polymers. The result may support the concept of chain shrinking as the origin of the nonlinear viscoelasticity.

The difference of the function $h(\gamma)$ for the two polymers may be of some interest. The values for the branched polymer are in better agreement with the theoretical values than those for linear polymers are. The deviation for the linear polymers has been observed consistently for many systems,^{2,4,5)} and is not likely to be due to an experimental error. One may rationalize the result of Fig. 5 as follows. The good separation between the reptation process and the shrink process is a basic presumption for the development of the viscoelasticity theory based on the tube model.⁴⁾ Obviously, the reptation process is highly hindered for the branched polymer, so that the shrink process may proceed ideally without a disturbance from the diffusional motion. Possibly the shrinking does not proceed ideally for the linear polymers for some unknown reasons and this causes the slight deviation between the theoretical and observed values of $h(\gamma)$.

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